

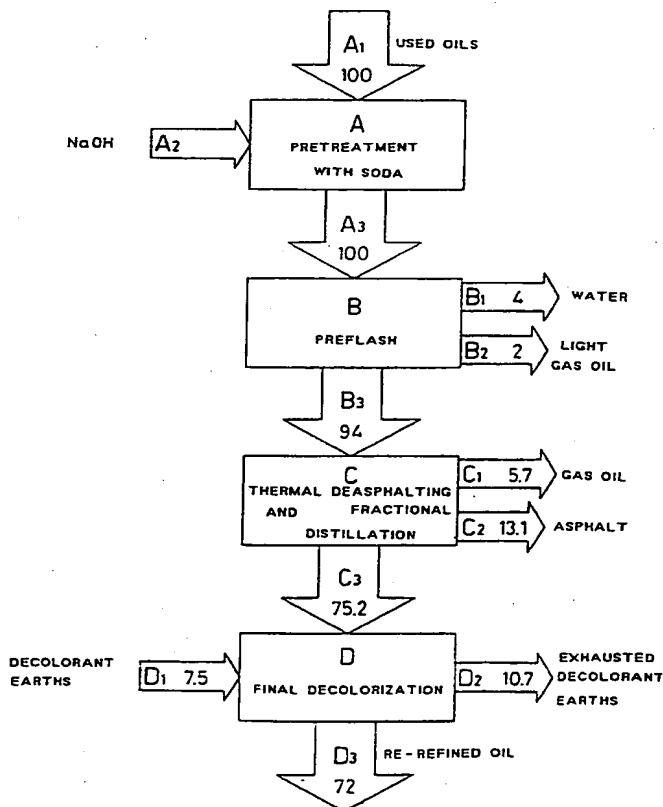


## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<b>(21) International Application Number:</b> PCT/EP93/02628 <b>(22) International Filing Date:</b> 28 September 1993 (28.09.93) <b>(30) Priority data:</b> MI92A002271 30 September 1992 (30.09.92) IT <b>(71) Applicant (for all designated States except US):</b> VISCO-LUBE ITALIANA S.P.A. [IT/IT]; Via Tavernelle, 5/7, I-20070 Pieve Fissiraga (IT). <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only) :</b> MIÑANA, José, Antonio, Gomez [ES/ES]; Reina Cristina, 11-3ª C, E-28014 Madrid (ES). SCHIEPPATI, Renato [IT/IT]; Strada Malaspina, 8, I-San Felice-Segrate (IT). DALLA GIOVANNA, Fabio [IT/IT]; Via Genova, 4, I-29100 Piacenza (IT).		<b>(74) Agents:</b> FAGGIONI, Marco et al.; Fumero Studio Consulenza Brevetti S.n.c., Via S. Agnese, 12, I-20123 Milano (IT). <b>(81) Designated States:</b> CZ, HU, RU, US, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). <b>Published</b> <i>With international search report.</i>

**(54) Title:** PROCESS TO RE-REFINE USED OILS**(57) Abstract**

Process to re-refine used oils, wherein the oils (A1) are initially subjected to a pretreatment (A) with a basic reagent (A2), then to a first preflash treatment (B) to eliminate the water (B1) and the most volatile fractions (B2) contained therein, and finally to a combined treatment (C) of fractional distillation and of purification to eliminate the high polymers and heavy metals, carried out into a single filled-type column (21), in order to obtain one or more fractions of re-refined oils (C3). The separation of the high polymers and heavy metals takes place, together with a cut of very heavy and viscous oils, from the bottom of the column (21) by means of a cyclone device (23). The re-refined oils (C3) are then subjected to a suitable decolorization treatment (D) and can be used as base oils for the production of lubrication oils.



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"PROCESS TO RE-REFINE USED OILS"

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The present invention concerns a high-yield and low-pollution process to re-refine used lubricating oils. In this particular branch of technique, the term "re-refining" means transforming used oils and fats - derived from engines or from other industrial uses - into base oils. Such base oils are then used, after mixing with suitable additives, as new lubricating oils having qualitative features which can be fully compared to those of the oils directly obtained by petroleum refinery.

The first industrial plants for re-refining used oils appeared in the nineteensixties, mainly in response to the considerable ecological problems resulting from the ground or water disposal of used oils. In the years that followed - due, on one hand, to the consumption increases and, on the other hand, to the costs of virgin oils of first refinery - the re-refined oils have been conquering an increasingly important position even as raw material. At present they are competitive, both as far as availability and as far as cost, with the oils directly obtained from petroleum.

The increasing economic interest in re-refined oils has led the governmental authorities to be more sensitive to the problem of their collection and concentration, by creating associations for collecting used oils, to which all the users are compelled to deliver their oils. This trend is up-to-date still in full expansion; in fact, in the EEC countries, against an annual consumption of lubricating oils amounting to about 4 millions of tons, and a corresponding theoretical quantity of recoverable used oils amounting to about 2.5 millions of tons, only 1.5 millions of tons of said used oils are actually collected and delivered to the re-refining centres, the remaining amount being disposed of in an uncontrolled manner, thus certainly harmful for the environment.

There are substantially two processes, mostly known and adopted in technique, to carry out the re-refining of used oils: the sulphuric acid process and the propane process. In both these processes, the used oils

are first of all freed from the water contained therein, and are then purified - with sulphuric acid or, respectively, with propane - to eliminate the other impurities present therein. These last ones substantially consist of compounds with high molecular weight contained in the oil additives, and of metals derived either directly by wear of the metallic parts, or indirectly by the metals present in the fuels or in the oil additives, as for example lead in petrols.

The sulphuric acid process was the first one to be conceived and adopted, but is now being dropped due to the considerable pollution problems which it involves. Said process essentially comprises the following steps, as shown on the block diagram of fig. 1:

- A - preflash, under moderate vacuum, of the used oils A1 in order to separate a head product, formed by water A2 and light hydrocarbons A3 (gas oil), from a tail product formed by the dehydrated oils A4;
- B - treatment of the dehydrated oils A4 with concentrated sulphuric acid B1, in an amount of 20-25% by weight, in order to obtain the extraction and then the decantation of the compounds with high molecular weight and of the heavy metals; and
  - separation of the acid sludges B2 with high content of oily fractions from the purified and acidized oils B3;
- C - neutralization of the oils B3 and decolorization of the same with a mixture C1 of lime and decolorant earths; and
  - filtration of said oils, allowing to obtain decolorized neutral oils C3 and to recover exhausted earths C2 soaked in high concentrations of oily fractions;
- D - hot vacuum distillation of the oils C3, with separation of the process water and of the gas oil D1 from the column head, and of the re-refined oils D2 into fractions of different viscosity from lateral outlets of the column; injection of superheated steam from the column bottom;
- E - final decolorization of the oils with decolorant earths E1, to obtain a lubricating base E3, with recovery of exhausted earths E2 soaked in

high concentrations of oily fractions.

Fig. 1 also indicates the fluid masses flowing into and out of each single block, with reference to an inlet flow-rate of used oils A1 equal to 100. This shows that the final yield of the sulphuric acid process does not even reach 60%.

A considerable amount of oils is in fact retained in the acid sludges B2 and cannot be easily recovered therefrom. The composition of said sludges is in fact quite varied and includes - besides sulphuric acid and the hydrocarbon compounds - polymeric compounds with high molecular weight, organic and inorganic compounds of sulphur, chlorine, nitrogen and phosphorus, and heavy metals as chromium, copper, zinc, iron, nickel and lead.

Seen the technological problems which an ecological elimination of this type of waste would involve, the solution still adopted at present in the existing plants is that of the disposal in dumps or quarries. At times, disposal is preceded by an operation to neutralize the acid sludges with lime, which however considerably increases their volume and the costs for their elimination, considering that 0.4 to 0.5 kg of lime are required for each kg of acid sludges. Also the incinerating technique is unadvisable, as it requires the installation and operation of complicated and costly equipment to depurate the smokes.

It is above all due to the pollution damages caused by the elimination of the acid sludges (less in volume, but certainly not less harmful than those produced by the direct elimination of used oils) that the installation of new re-refining plants, making use of sulphuric acid, has rapidly ceased as soon as the second of the known processes, making use of propane, has appeared on the market.

The block diagram of this second process is shown in fig. 2, in a way similar to that done for the above described sulphuric acid process; also in this case, the different flows into and out of the single blocks are indicated with reference to a feeding flow-rate of A1 equal to 100. In the propane process, the acid treatment step is totally replaced by an

operation B of clarification with liquid propane.

Said hydrocarbon can in fact be easily liquefied and has, in this liquid phase, a very low density. When mixed with the used oils, propane thus acts thereon as a thinning and fluidizing agent, allowing to easily obtain the separation of a first liquid fraction B1 with high viscosity, containing the high polymers and heavy metals - generally indicated by "asphalts" - from a second liquid fraction B2 consisting exclusively of the clarified and dehydrated oils. The plant of course provides for a depropanizing treatment of the liquid fraction B2, and for the recycle of the propane thus recovered.

The successive filtration step C with decolorant earths C1 is carried out with a hot treatment so that, as well as recovering the exhausted earths C2, one also recovers a gaseous fraction C3 consisting of a minor portion of the gas oil contained in B2. The remaining part of gas oil abandons this block together with the decolorized oils C4 and is recovered in D1 in the successive distillation step D. The distillation step D and the final decolorization step E are fully identical to those previously described with reference to the sulphuric acid process.

The propane process represents a considerable improvement in respect of the sulphuric acid process, both as far as yield - which has risen to about 68% - and as far as pollution, which is notably reduced. Nevertheless, also this process has some inconveniences. To start with, the handling of propane creates problems of safety for the workers on account of its high explosiveness; furthermore, in spite of the above mentioned depropanizing treatments, the heavy fraction of asphalts B1 still shows traces of propane. This even small quantity of propane is sufficient to prevent the use of such asphalts in potentially interesting fields as the roadway or the building field. The presence of propane is in fact apt to notably increase the inflammability of asphalts, making it on one hand difficult to handle them when bituminous roadbeds have to be formed, and preventing on the other hand one of the most interesting uses thereof in the building field, namely the forming of sealing coatings. In

fact, sealing coatings realized with such asphalts could not - as usually done - be flame-welded, without risking fires.

Consequently, in the propane process, the asphalts should be considered in every respect as a waste product, which can be disposed of - by previous dilution with gas oil so as to make it sufficiently fluid - only as fuel having a good heat value but a high pollution rate. A typical use thereof is in the casehardening furnaces, already provided with special equipment to depurate the smokes and apt to eliminate also the pollutants present in such asphalts.

Finally, from the energetic point of view, the propane process is far more demanding than the sulphuric acid process, both in terms of electric energy consumption and in terms of fuel consumption to produce the process steam and to heat the oils.

In recent years, a third type of process has been introduced wherein the used oils, after the conventional dehydration step, are subjected to a thin-film distillation process. In said continuous process, the used oils are sent to an axial rotor of a distillation column and, from said rotor, they are sprayed onto the inner walls of the column, which are kept at high temperature by a diathermic fluid flowing into a lining of said column.

In contact with the column wall, the light vaporizable fraction of the oils instantly turns into a gas phase, while the heavy fraction stays liquid and collects onto the bottom of the column. The vaporized fraction is then collected and fractionated into the desired cuts in a successive fractionating column.

This continuous process allows interesting yields, but involves a series of inconveniences which limit its diffusion. To start with, it requires a pretreatment to purify the used oils so that it can be continued for a fairly long time without having to provide for extra cleaning operations; in particular, the presence of the rotor makes this process very delicate as far as fouling is concerned, and makes periodic maintenance very costly as far as cleaning is concerned. In the second place, said

process involves high capital and running costs which do not make it economically competitive in respect of the propane process. Finally - since the height of the thin-film distillation column has to be limited due to the need to fully draw out the rotor for its cleaning - when the process has to be applied to high feeding flow-rates, it requires the use of several parallel columns, without being able to achieve any scale saving.

The inventors of the present patent have thus proposed to themselves the object of preparing a process to re-refine used oils: allowing to reduce or fully abandon the use of reagents which are difficult to eliminate or anyhow harmful for the environment or dangerous for human safety; apt to be carried out with a simple and compact plant, not weighing on the production costs and also allowing to reduce energy consumption; apt to be carried out in a completely static plant, the single components of which should not include any moving parts, highly subject to great fouling problems typical of the used oil treatments; and, finally, apt to increase the still not satisfactory yields of the known processes, both for what concerns the quantity and quality of the recovered oils, and for what concerns the possibility to utilize the by-products in economically profitable uses, apt to make said process globally more advantageous.

According to the present invention, said objects are reached with a process to re-refine used oils - of the type in which said oils are subjected to a first preflash treatment to eliminate the water and the most volatile fractions contained therein, to a purification treatment to eliminate the high polymers and heavy metals, to a fractional distillation treatment to obtain one or more oil fractions for use as lubricating bases, and finally to a decolorization treatment - characterized in that:

- said fractional distillation treatment is carried out into a single filled-type column;

- said purification treatment is carried out in three successive steps: a first step of pretreatment wherein, before said preflash treatment, a highly basic reagent is added and mixed with the oils; a second step wherein, before the fractional distillation treatment, the oils



resulting from the preflash treatment are decanted; a third step wherein a heavy liquid fraction containing said high polymers and heavy metals is discharged from the base of said fractionating column.

Further characteristics and advantages of the re-refining process according to the present invention will anyhow be more evident from the following detailed description of a preferred plant, into which said process is carried out, illustrated on the accompanying drawings, in which:

Fig. 1 is a block diagram, illustrating the known-type sulphuric acid re-refining process;

Fig. 2 is a block diagram, illustrating the known-type propane re-refining process;

Fig. 3 is a block diagram, illustrating the process to re-refine used oils according to the present invention;

Fig. 4 is a diagram of the plant to carry out the process of the invention, wherein the basic reagent addition step and the preflash step are illustrated in further detail; and

Fig. 5 is a diagram of the plant to carry out the process of the invention, wherein the fractional distillation step and the step to separate the heavy fraction containing the high polymers and heavy metals are illustrated in further detail.

The process to re-refine used oils, according to the present invention, differs from the known processes for the fact of having notably simplified the purification treatment and of having combined into a single column all the distillation treatments (which, in the known processes, are carried out into several cascade columns) as well as the operation to separate a heavy fraction containing the high polymers and heavy metals. Moreover, this last separation is carried out by means of a cyclone device positioned in the lower part of the distillation column, which does not provide for the use of any movable parts and is therefore not subject to problems of fouling or blocking, caused by the high viscosity and the special composition of the materials being treated.

Fig. 3 reports a block diagram illustrating the main steps of the process according to the invention. Like the similar diagrams of figs. 1 and 2 - illustrating the known processes and already discussed heretofore - this diagram indicates the fluid masses flowing into and out of the single blocks, with reference to a feeding flow-rate of used oils A1 equal to 100.

As said above, the treatment to purify the used oils from the high polymers and heavy metals includes a pretreatment A with a basic reagent. A reagent preferred for this purpose is NaOH, which is added in A2 and mixed with the oils A1 before the preflash treatment. Said pretreatment does not act directly on the above pollutants, but helps on one hand to saponify the fatty acids present therein, favouring their precipitation, and on the other hand to neutralize the chlorine present both in bound and in free form. The saponification of the fatty acids, besides facilitating their elimination by decantation - hence improving the flowability of the system - destroys their volatility and thus prevents said acids from turning into vapour in the distillation column, thereby polluting the oils both directly and with the polluting parts eventually bound thereto. The neutralization of chlorine also preserves the plant from dangerous phenomena of corrosion, lengthening its working life.

The successive preflash treatment B involves - as in the processes of known technique - the separation of an oily water flow B1 and a gas oil flow B2. Before being sent to the successive step, the flow of dehydrated oils B3 resulting from the preflash treatment is left to rest for a length of time sufficient to obtain the decantation of the saponified or flocculate parts.

The flow of oils, thus treated, is sent to a treatment of thermal deasphalting and of fractional distillation C which simultaneously involves, both the separation of a light phase C1 containing gas oil and of a heavy phase C2 containing the high polymers and heavy metals, and the fractionation of the oils into three cuts C3 of different density. The three cuts thus obtained, suitably purified with a stripping treatment,

are sent to the final decolorization treatment D - known per se - into which is fed a flow of decolorant earths D1 and from which the flow of exhausted earths D2 is removed, thereby obtaining a main flow of re-refined oils D3, with a very high yield equal to about 72%. With an additional process to recover the oils into which the exhausted earths D2 are soaked, the yield can even rise to 75%. Alternatively, the decolorization of the re-refined oils D3 can be carried out with a hydrogen treatment, also perfectly known in technique.

The process steps of blocks A, B and C are now described in detail with reference to the plant illustrated in figs. 4 and 5.

Fig. 4 reports the blocks A and B. The used oils A1 are fed through the pump 1 into the preflash column 2. Into the outlet of said pump is also fed the basic reagent A2, with a flow-rate controlled by the metering pump 3. As specified above, said reagent preferably consists of NaOH and is added, as a 30% solution, in an amount such as to settle the pH of the used oils - at the outlet of column 2 - at a value between 10 and 13, and preferably between 11.8 and 12.2. The flow-rate of the pump 3 is thus preferably regulated automatically by a pH control device 4 positioned at the outlet of column 2.

The used oils A1 and the reagent A2 are then thoroughly mixed into a line mixer 5, and are subsequently preheated to a temperature of about 120°-140°C into the exchanger 6 fed by the steam line VAP.

The preflash column 2 is kept under a moderate vacuum degree, equal to about 200 mmHg, by means of an ejector 7 fed by the same steam line VAP. The flow A3 fed into column 2 is then separated into a vapour phase, containing water and gas oil, and into a liquid phase, containing the dehydrated oils and the pollutants. The vapour phase is condensed by the water-cooled condenser 8a and sent to the gravity separator 9. The same separator 9 also receives the steam let out from the ejector 7, after it has been condensed in the condenser 8b.

The separator 9 provides to separate an incondensable gaseous phase GAS - which is sent to a high-temperature burner, so as to destroy any

gaseous pollutants present therein - from the two already described liquid flows B1 and B2. The water flow B1, slightly oil-polluted, is sent to a biological depuration plant together with the process waters let out of the other parts of the plant. This is actually the only waste product of the process according to the present invention, which does not exceed 4% by weight of the feeding and which creates no particular problems for its proper elimination. The gas oil B2 - of excellent quality, seen that the oils have not been subjected to treatments with polluting reagents - can be introduced in the normal trade channel of fuels.

The bottom product B3 of the column, eventually condensed by a cooling coil 10, is sent by a pump 11 into a collection tank 12. The dimensions of the tank 12 and the positioning of the inlet and outlet pipes are calculated so that the stay time therein of the flow B3 is at least 48 hours. In this way, the saponified fatty acids and the other flocculate parts - thanks to the treatment with NaOH - are able to decant on the bottom of the tank 12, from which they are periodically removed through the drain 13, entraining therewith a certain amount of impurities.

Fig. 5 illustrates the thermal deasphalting and fractional distillation treatments carried out on the flow B3 of dehydrated oils. Said oils are first of all heated to a temperature of about 360°C in the methane gas furnace 20. The oils are then fed to the bottom of the fractionating column 21, into which is kept a vacuum degree of at least 10-20 mmHg (at the top of the column), thanks to a main ejector 22a, series connected to two secondary ejectors 22b and 22c, all fed by the VAP line. More precisely, the heated and partially vaporized oils are sent to the top of a cyclone device 23, positioned in the lower part of the column 21 and consisting of an open-spiral channel leading down around a large central tube which connects the bottom part of the column to its part immediately above.

At the inlet of column 21, the flow B3 almost totally vaporizes and the cyclone device 23 allows a perfect and complete separation of the gaseous phase from the liquid phase, which contains the very heavy oil

fractions and all the pollutants consisting of the high polymers and heavy metals. This liquid phase C2, commonly called "asphalts", is sent to the collection tanks through a pump 24.

The vapour phase, released from the cyclone 23, moves up along the column 21, meeting four successive filling packs 25, positioned over respective collection plates 26, which allow - in known manner - to let through the vapour phase which rises towards the top, and to retain the liquid which has condensed. The fractionating column 21 of the present invention has been conceived so as to allow cutting the inlet flow into a head fraction, substantially containing the process vapour and the gas oil, and into three intermediate cuts (indicated by C3/I, C3/II and C3/III) of re-refined oils of different density, ready for the different commercial uses, as well as into the already described tail fraction C2.

To obtain this result, the filling should have a very low flow resistance (5-10 mm Hg at most, for each pack) and a high gas/liquid contact surface. An extremely positive result has been obtained by using a metal filling consisting of side-by-side, superposed, accordion-folded metal sheets, forming zig-zag channels allowing the vapours to rise, of average size from 1 to a few centimeters. A filling of this type, made from stainless steel, is produced by Glitsch Italiana - Campoverde di Aprilia (Latina), Italy - and is known on the market under the trade name GEMPACK.

The liquid cut collected on the top plate 26a, namely the plate positioned under the first filling pack 25, is reflowed by the pump 27a into a column zone just below said plate and, after having been cooled into the water exchanger 28, it is sent to the head of the column 21. The portion exceeding the requirement of the reflux is collected in C1, as gas oil, to be put on the market together with the flow B2 separated in the previous preflash step.

The liquid cuts collected on the two underlying plates 26b and 26c are reflowed into the column zones just below said plates, through the circulation pumps 27b and, respectively, 27c. The portion of these two

liquid cuts exceeding the reflux requirements are sent to separate parts of a stripping column 29 formed of three different sections, into one of which also flows directly the cut collected on the bottom plate 26d. In the three sections of the stripping column 29 the three cuts are purified even further, in a countercurrent of steam fed from the VAP line and superheated in the furnace 20.

The cuts collected in the stripping column 29 are finally sent to the collection tanks by the pumps 30b, 30c and 30d, after cooling into air coolers 31.

The flows coming from the main ejector 22a and from the secondary ejectors 22b and 22c, containing process vapour, incondensable gases and gas oil vapours, are condensed into the water condensers 32 and then collected into a gravity phase separator 33. In the separator 33, the gas oil phase escaped from the head of the column 21 is separated from the process water phase and from the incondensable gases. The gas oil is fed in C1; the water flow 34 is recycled to the steam production boilers after having possibly undergone a depollution treatment; while the incondensable gases are sent into GAS and then into a combustion furnace to eliminate any possible polluting gases.

The cuts of re-refined oils thus obtained - heavy oils C3/I, middle oils C3/II, light oils C3/III - are sent to a final decolorization plant, wherein said oils are subjected - in known manner - to a decolorization treatment with decolorant earths or with hydrogen, so as to make them suitable for the market.

The asphalt flow C2 - thanks to the total absence of solvents and for the very fact of containing, as vehicle of the pollutants, a fraction of very heavy and viscous oils (bright stock) - can be marketed, in an economically interesting way, to form bituminous roadbeds, to which it confers special elastomeric and deadening characteristics.

The process to re-refine used oils according to the present invention is thus particularly advantageous compared to the processes of known technique. In fact, apart from being carried out into a considerably

simple plant, which thus involves less installation costs, there is also a reduced need for periodic maintenance, thanks to the basic purification pretreatment as well as to the complete absence of movable parts.

Also as far as running costs, the process of the present invention is highly competitive, as results from the following comparison Table reporting the costs of the expendable products, as well as the costs for the disposal of the waste products, which - as can be seen - are altogether 25% in respect of the costs met with the sulphuric acid process, and 60% in respect of those met with the propane process.

Finally, the waste products of the process merely consist of the water separated from the oils in the preflash step. Said water forms a very small fraction - about 4% - of the initial feed A1, and anyhow creates, as seen above, no ecological problems as far as disposal is concerned.

T A B L EPRODUCTS

(per ton of used oil)

TYPE OF PROCESS

		Sulph. Acid	Propane	Invention
<u>Expendable:</u>				
Natural gas	SM <sup>3</sup>	160.2	215.8	98.61
Electric current	Kwh	75.6	102	58.53
Additives	US\$	3.44	4.9	2
Reagents	Kg	-	-	17
Propane	Kg	-	5	-
Acid	Kg	178.3	-	-
Nitrogen	Kg	2.5	2.5	2.35
Decolorant earths	Kg	88.9	119.4	81.5
Paper, filters, etc.	US\$	2.08	1	2
<u>To be disposed of:</u>				
Exhausted earths	Kg	239.87	190.67	131
Acid sludges	Kg	356.25	-	-
<u>TOTAL COSTS</u>		US\$ 200	100	60
(per ton of used oil)				
<u>YIELDS</u>		58.2%	68.79%	72%
<u>TOTAL COSTS</u>		US\$ 344	145	83
(per ton of re-refined oil produced)				

Reference values:

- Natural gas	US\$/Sm <sup>3</sup>	0.18
- Electric current	US\$/Kwh	0.095
- Reagents	US\$/Kg	0.16
- Propane	US\$/Kg	0.45
- Acid	US\$/Kg	0.12
- Nitrogen	US\$/Kg	0.37
- Decolorant earths	US\$/Kg	0.25
- Disposal of exhausted earths	US\$/Kg	0.056
- Disposal of acid sludges	US\$/Kg	0.28



CLAIMS

1) Process to re-refine used oils, of the type in which said oils (A1) are subjected to a first preflash treatment (B) to eliminate the water (B1) and the most volatile fractions (B2) contained therein, to a purification treatment to eliminate the high polymers and heavy metals, to a fractional distillation treatment (C) to obtain one or more oil fractions for use as lubricating bases, and finally to a decolorization treatment (D), characterized in that:

- said fractional distillation treatment (C) is carried out into a single filled-type column (21);

- said purification treatment is carried out in three successive steps: a first step of pretreatment (A) wherein, before said preflash treatment (B), a highly basic reagent (A2) is added and mixed with the oils (A1); a second step wherein, before the fractional distillation treatment (C), the oils (B3) resulting from the preflash treatment (B) are decanted; a third step wherein a heavy liquid fraction (C2) containing said high polymers and heavy metals is discharged from the base of said fractionating column (21).

2) Process as in claim 1), wherein said filled-type fractionating column (21) is a four-stage column with an overall flow resistance not exceeding 40 mm Hg.

3) Process as in claim 1), wherein said filled-type fractionating column (21) is a four-stage column with an overall flow resistance not exceeding 20 mm Hg.

4) Process as in claim 1), wherein the filling (25) of said column (21) consists of side-by-side, superposed, accordion-folded metal sheets.

5) Process as in claim 1), wherein the oils (B3) resulting from the preflash treatment (B) are fed in a cyclone device (23) positioned in the lower part of said fractionating column (21), wherein they are separated into a gaseous fraction which is sent to the upper part of said column (21), and into said heavy liquid fraction (C2) containing high polymers

and heavy metals which is discharged.

6) Process as in claim 1), wherein said fractionating column (21) comprises no movable portions, even in the lower part where the oil cyclonation takes place.

7) Process as in claim 1), wherein said highly basic reagent (A2) is NaOH.

8) Process as in claim 7), wherein said reagent (A2) is introduced in an amount sufficient to keep the pH of the dehydrated oils, coming from the preflash step, in a range between 10 and 13 and, preferably, between 11,8 and 12,8.

9) Process as in claim 1), wherein said decantation is carried out in a tank (12), positioned between the preflash column (2) and the fractionating column (21), with a stay time of at least 48 hours.

10) Process as in claim 1), wherein the distilled oil fractions (C3/I,II,III) drawn from the fractionating column (21), before undergoing the decolorization treatment (D), are treated in a stripping column (29).

11) Process as in claim 1), wherein said decolorization treatment (D) is carried out with decolorant earths (D1).

12) Process as in claim 1), wherein said decolorization treatment (D) is a hydrogen treatment.

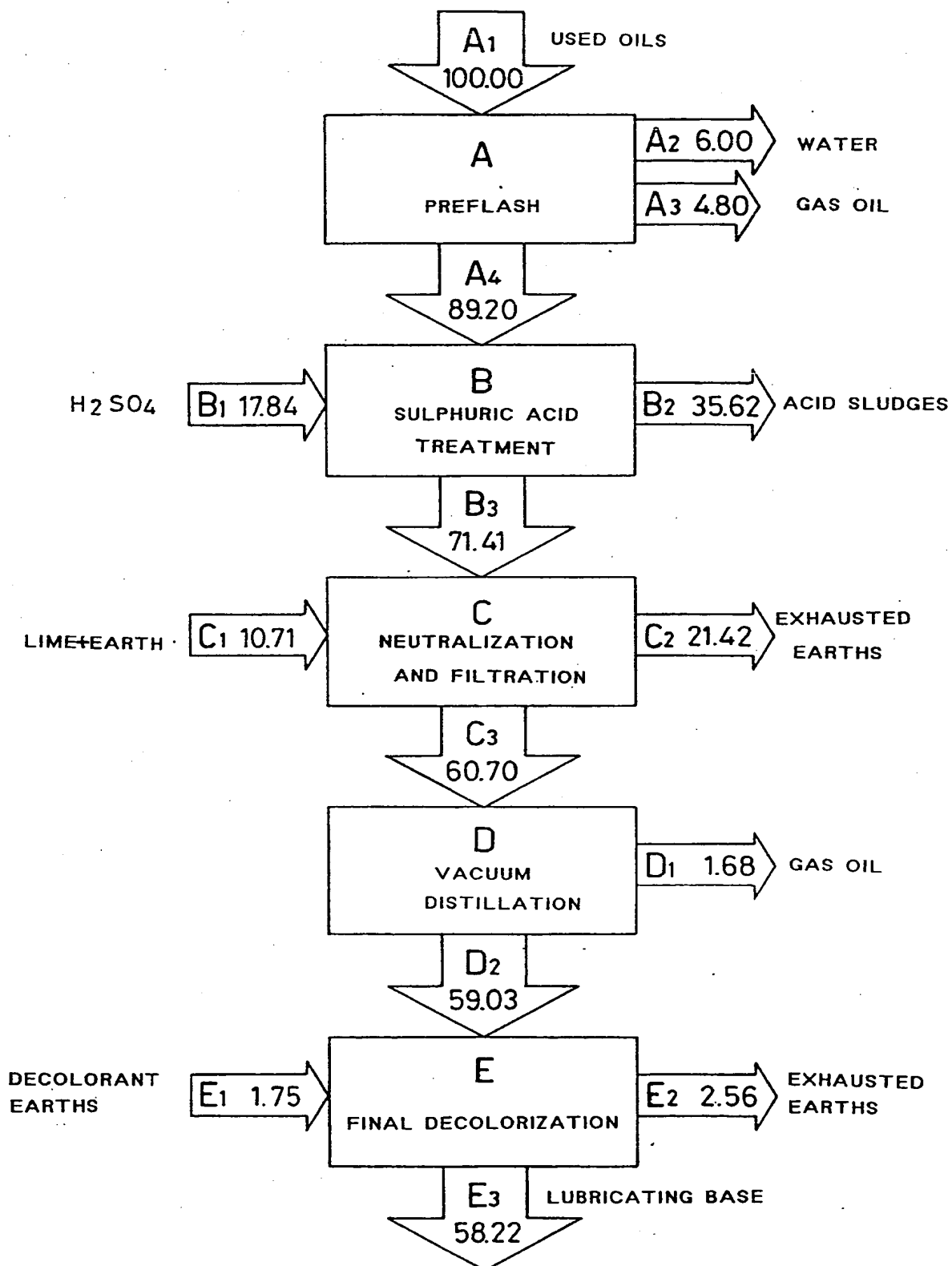


FIG. 1

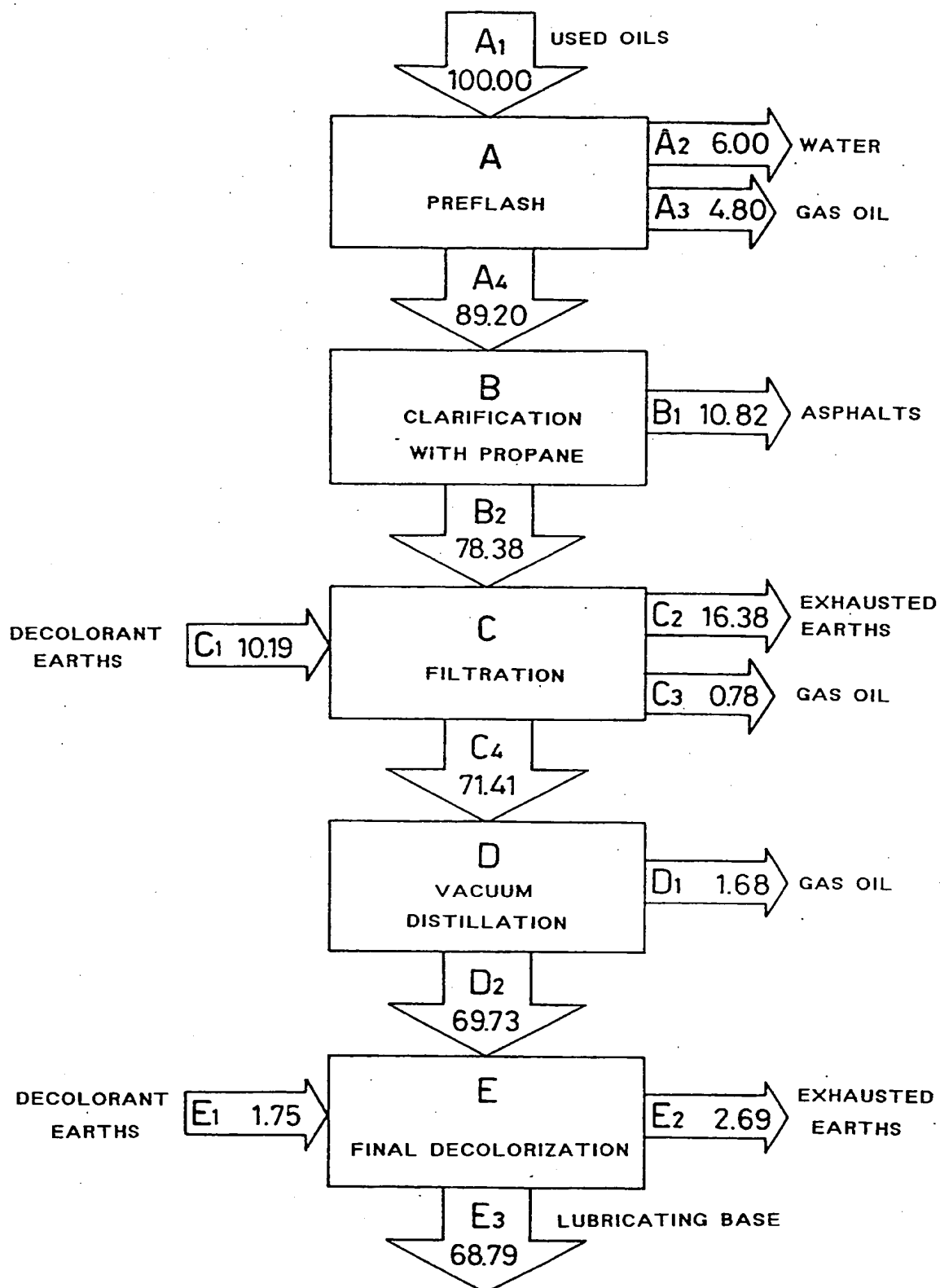


FIG. 2

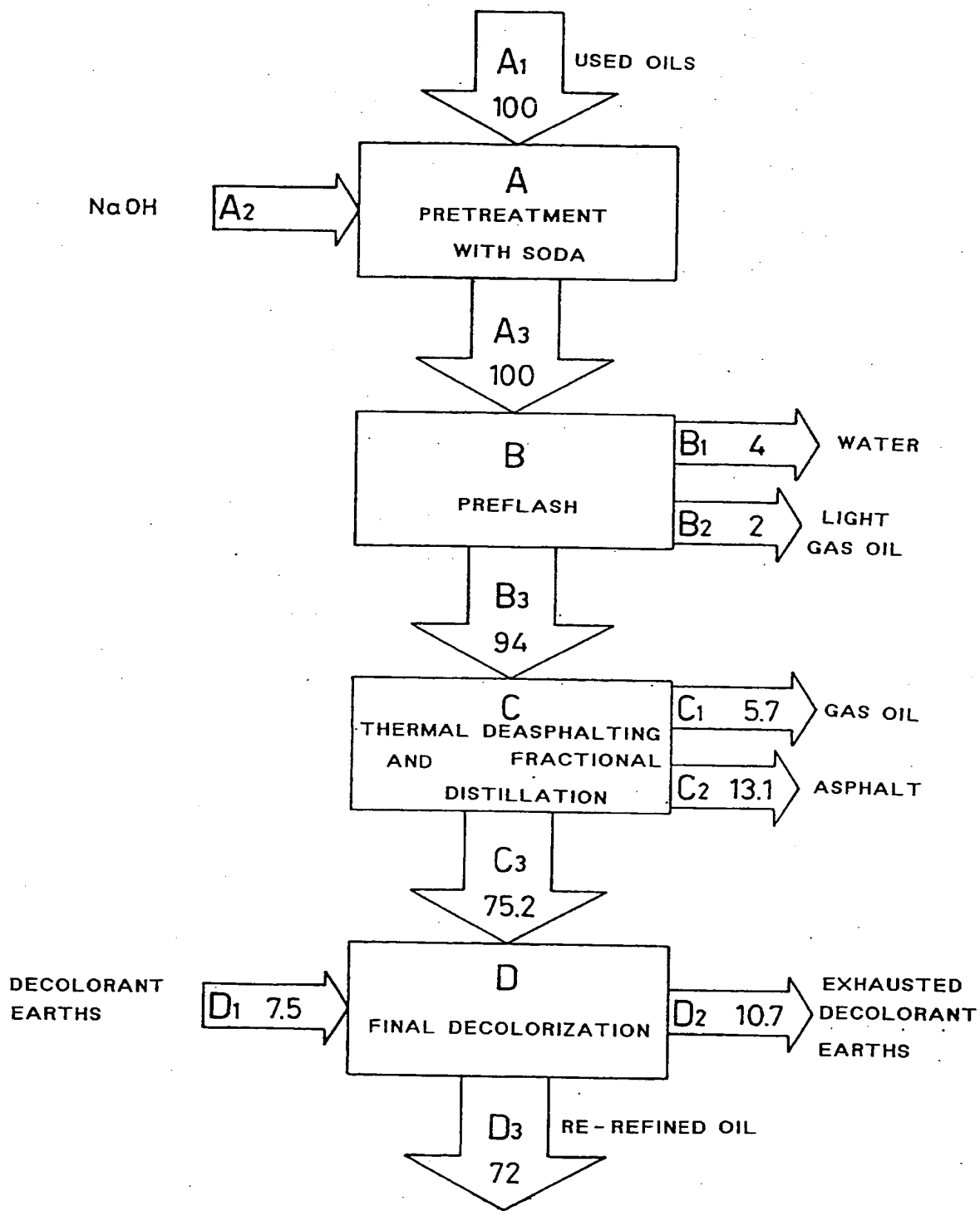


FIG.3

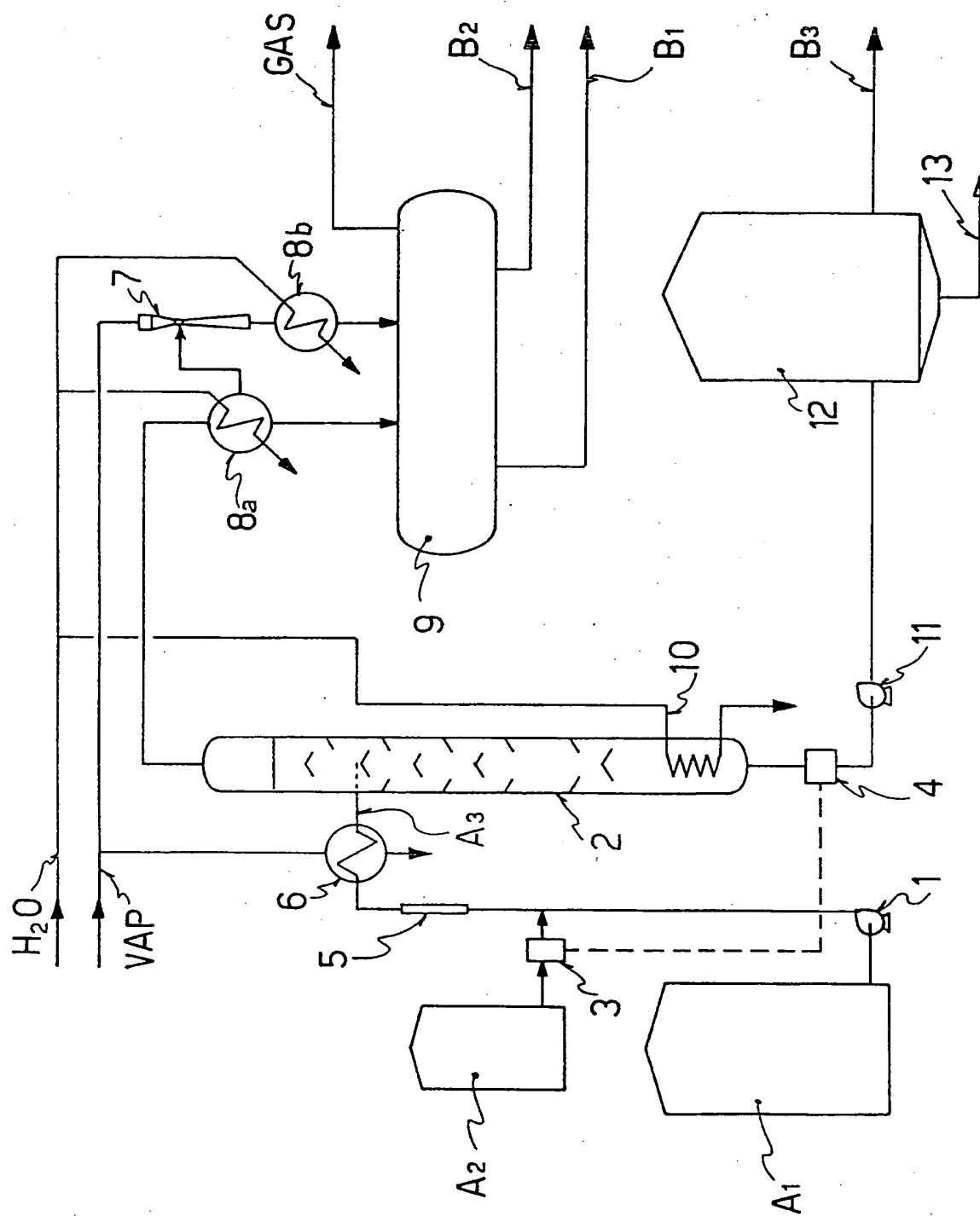


FIG. 4

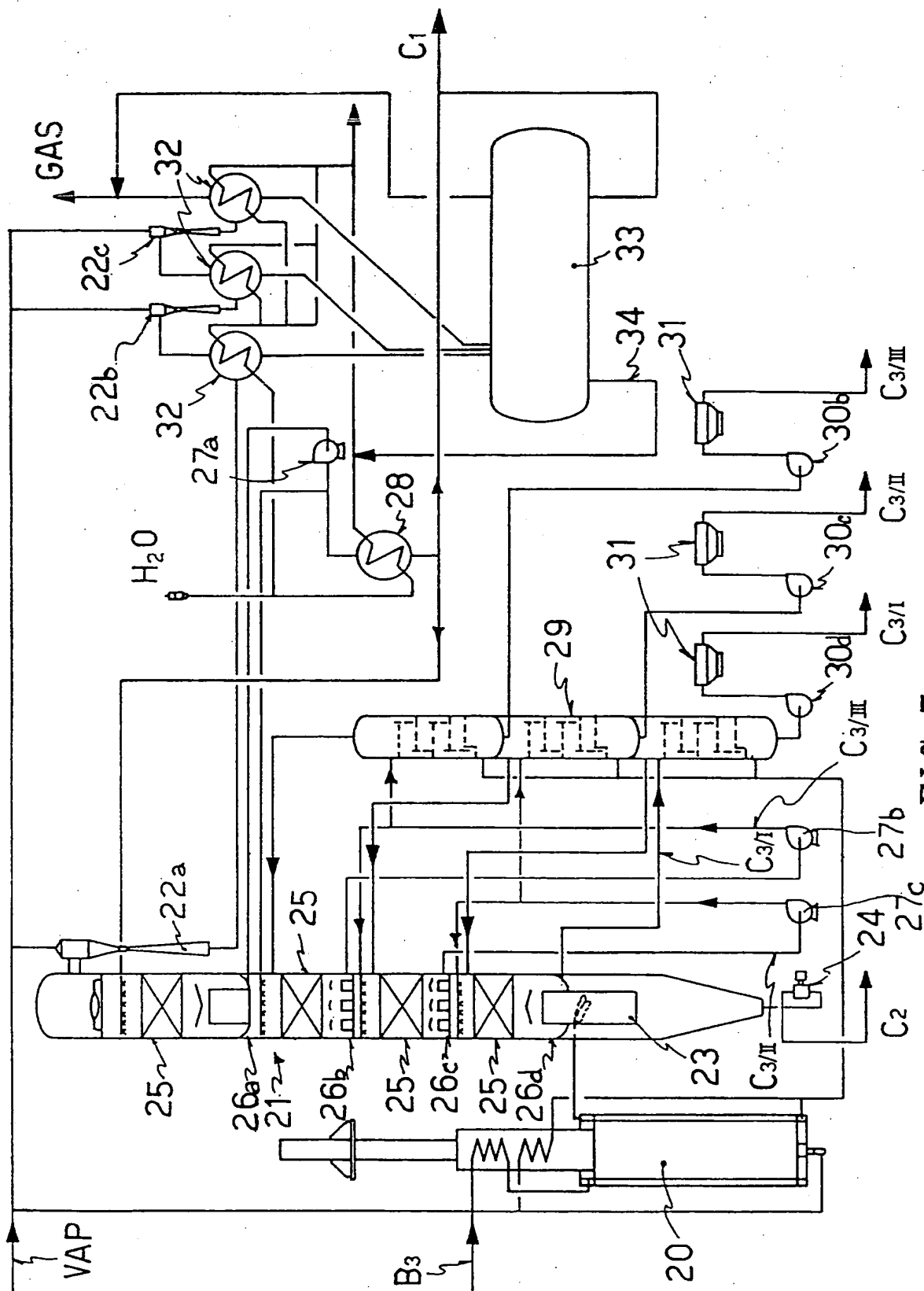


FIG. 5

## INTERNATIONAL SEARCH REPORT

Intern. Application No

PCT/EP 93/02628

A. CLASSIFICATION OF SUBJECT MATTER  
 IPC 5 C10M175/00 C10G53/12 C10G67/10

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 5 C10M C10G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	GB,A,2 022 131 (DEUTSCHE GOLD UND SILBER SCHEIDEANSTALT) 12 December 1979 see page 4; example 3 see page 8; example 5 ---	1,7,9, 11,12
A	GB,A,2 099 847 (PHILLIPS PETROLEUM COMPANY) 15 December 1982 see claim 1 ---	1,6,12
A	US,A,3 625 881 (J.M CHAMBERS) 7 December 1971 see claim 1 see column 6, line 3 - line 15; figure 2 ---	1,4,7
A	FR,A,2 302 335 (ADOLFS SCHMIDS ERBEN AKTIENGESELLSCHAFT) 24 September 1976 see page 3, line 17 - line 27 see page 24; figure 1 ---	1,12
-/--		

☒ Further documents are listed in the continuation of box C.

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Date of the actual completion of the international search

21 December 1993

Date of mailing of the international search report

1 3. 01. 94

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO,A,92 15659 (MYRVOLD) 17 September 1992 see claim 1 ---	1,5
A	FR,A,886 208 (YRJO TAIPALE) 8 October 1943 see claim 1 ---	1,11
A	US,A,3 565 791 (K. URQUHART) 23 February 1971 see column 3, line 35 - line 41 see column 3, line 52 - line 54 ---	1,10
A	US,A,3 923 643 (R.W LEWIS) 25 January 1965 see column 5, line 25 - line 32 see column 5, line 49 - line 54 ---	1
A	US,A,4 140 212 (R.H O'BLASNY) 20 February 1979 see column 6, line 1 - line 6 see column 7, line 16 - line 47; figure 4 -----	1,5

## INTERNATIONAL SEARCH REPORT

 Intern. Appl. Application No  
 PCT/EP 93/02628

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
GB-A-2022131	12-12-79	DE-A-	2818521	08-11-79
		AU-A-	4445079	01-11-79
		FR-A-	2424314	23-11-79
		JP-A-	54142206	06-11-79
		SE-A-	7903696	28-10-79
		US-A-	4252637	24-02-81
-----				
GB-A-2099847	15-12-82	BE-A-	893434	07-12-82
		CA-A-	1174630	18-09-84
-----				
US-A-3625881	07-12-71	NONE		
-----				
FR-A-2302335	24-09-76	DE-A-	2508713	09-09-76
		GB-A-	1526334	27-09-78
		JP-A-	51111209	01-10-76
		US-A-	4097369	27-06-78
-----				
WO-A-9215659	17-09-92	AU-A-	1562892	06-10-92
-----				
FR-A-886208		NONE		
-----				
US-A-3565791	23-02-71	NONE		
-----				
US-A-3923643	02-12-75	NONE		
-----				
US-A-4140212	20-02-79	NONE		
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